The controlled polymerization of poly(cyclopentadithiophene)s and their all-conjugated block-copolymers

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Abstract. In this manuscript, the Kumada catalyst transfer polymerization (KCTP) of cyclopenta[2,1-*b*;3,4-*b'*]dithiophene (CPDT), a monomer consisting of two fused thiophene entities, is investigated. It is shown that this polymerization follows a controlled chain-growth mechanism. Furthermore, the formation of block-copolymers with poly(3-alkylthiophene)s is investigated, and it is shown that these block-copolymers can be formed if 3-alkylthiophene is used as the first block and CPDT as the second. The resulting all-conjugated block-copolymers consist of two blocks with substantially different electronic and physical properties and it is shown that the blocks influence each other, resulting in a unique material with different properties compared to a blend.

INTRODUCTION

A vast amount of research has been, and is still being, performed on conjugated polymers (CP) because of their application as flexible electronics, like e.g. flexible television screens, solar cells, etc.[1–3] Within the research area of CPs, there has been a clear synthetical evolution, starting from electrochemical and oxidative polymerizations, towards transition metal catalyzed polymerization mechanisms.[4–7] Herein, the transition metal catalyst forms a new C-C bond between two entities of which one carries a carbon-halogen bond, and the other one is, most frequently, an organometallic monomer system, although recent research also focuses on direct arylation where coupling takes place with a C-H bond instead of with an organometallic monomer.[8–11] The traditional transition metal catalyzed polymerization mechanisms generally proceed via a step-growth mechanism, and are still the most obvious choice for the synthesis of alternating copolymers. However, for other materials, it can be a great benefit to step away from these difficult-to-control polymerization mechanisms, towards a (controlled) chain-growth mechanism, in which polydispersities can be low, and molecular weights can be controlled. Moreover, this also enables the synthesis of fully conjugated block-copolymers and other supramolecular structures in one-pot polymerizations. A first and widely used protocol was established by the research groups of Yokozawa and McCullough in 2004, which used a Ni(dppp)Cl_2-catalyst (dppp= 1,3-bis(diphenylphosphino)propane) in combination with organomagnesium monomers.[12–15] Later on, also Suzuki-Miyaura coupling reactions were used to achieve a controlled chain-growth polymerization mechanism.[16–21] Furthermore, a controlled chain-growth mechanism based on a *N*-heterocyclic carbene-ligated Pd-catalyst was obtained and also a Ni$(acac)_2$/dppp catalyst was successfully used to obtain a controlled chain-growth

mechanism.[22,23] Finally, also a controlled chain-growth polymerization mechanism based on Rieke-type coupling reactions has been reported using an external initiator.[24,25]

These polymerization mechanisms have, up to now, resulted in the controlled polymerization of poly(3-alkylthiophene)s (P3AT)[12,15], poly(fluorene)s[23,24,26], poly(phenylene)s[27], poly(pyrrole)s[28], poly(pyridine)s[29], poly(bithienylmethylene)s[30], poly(selenophene)s[31,32] and poly(dithieno[3,2-*b*;2',3'-*d*]silole)s[33]. Also an array of block-copoly(3-alkylthiophenes) has been synthesized by polymerizing monomers with identical backbone units, but with different side-chains.[34–49] All-conjugated block-copolymers consisting of two different monomer systems are, on the other hand, scarce and those who are synthesized using a one-pot polymerization method, are even scarcer.[18,24,26,31–33,50–61] As a consequence, the straightforward synthesis of these all-conjugated block-copolymers by one-pot polymerization methods is a great current challenge, as it has been demonstrated that the resulting materials show promising properties for their use in organic electronics.[62]

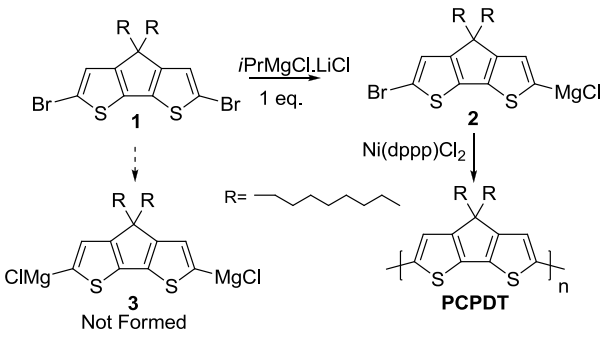
Cyclopenta[2,1-*b*;3,4-*b'*]dithiophene (CPDT) is a monomer building block consisting of a thiophene dimer which is bridged in the 3,3'-position by a non-conjugated carbon atom. This monomer system has already been the subject of quite an amount of research and is at the moment especially popular for the use in alternating donor-acceptor low-bandgap copolymers.[63–66] The CPDT homopolymers (PCPDT) show a decreased bandgap (~1.8 eV) in comparison with poly(3-hexylthiophene) (P3HT), are very soluble in organic solvents and exhibit high extinction coefficients at its absorbance maximum (~590 nm).[67] These PCPDT homopolymers have, up to now, mostly been synthesized using the step-growth polycondensation methods described above. Coppo *et al*. have also synthesized PCPDT using both a GRIM and a Rieke type monomer formation, in combination with, respectively, a Ni(dppp)Cl_2 and a Ni(dppe)Cl_2 catalyst, however,

the nature of this polymerization was not clarified.[68] In this work, the controlled nature of the Kumada catalyst transfer polycondensation (KCTP) mechanism, applied on these CPDT-molecules is investigated in detail. Furthermore, the possibilities towards all-conjugated 3-hexylthiophene-CPDT block-copolymers are explored.

RESULTS AND DISCUSSION

Monomer synthesis

The precursor monomer (**1**) was synthesized according to existing literature procedures.[67,68] Starting from this precursor monomer, the actual monomer can be formed by a Grignard Metathesis (GRIM) reaction. Due to the symmetric nature regioregularity is no issue, but the longer distance between the two C-Br bonds (similar to a thiophene dimer) may result in a weaker deactivation of the remaining C-Br bond by the C-MgX bond. Therefore, the question arises whether this GRIM reaction can be selective, and if the right monomer (**2**) can be quantitatively formed without the bireacted side product **3** (Scheme 1).



Scheme 1. Reactions of the CPDT precursor monomer.

The monomer conversion is monitored using ^{1}H NMR spectroscopy in $CDCl_3$: after GRIM reaction with 1 equivalent of *i*-PrMgCl·LiCl for 30 min, the monomer mixture was quenched in H_2O, hereby replacing all –MgX functionalities by H-atoms, and the ^{1}H NMR spectra of the

reaction mixture and the products that can, theoretically, be present (**1**, **2** and **3**) are compared (Figure 1). From these spectra, it is clear that only **1** and **2** are present, and that there is no formation of the bireacted entity **3**.

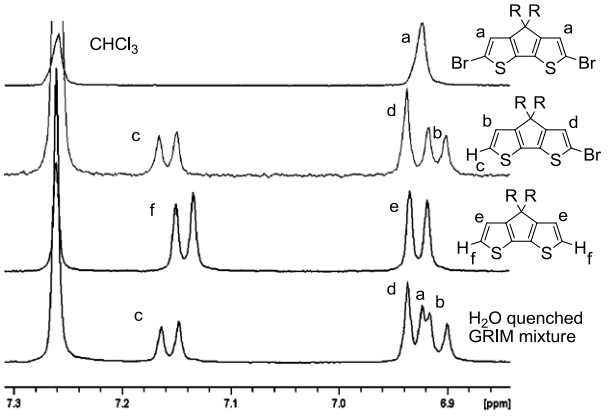


Figure 1. Aromatic region of the ^{1}HNMR spectra of the CPDT-monomer derivatives.

Nonetheless, the amount of unreacted monomer **1** is still quite high, so further optimization is necessary, which was performed by varying the concentration and temperature. An overview of the used conditions is given in Table 1. A first observation is that performing a GRIM at a higher temperature consistently yields a lower conversion in comparison with the GRIM at room temperature. Second, a concentration of 0.1 M appeared to be optimal, with lower conversions for both lower and higher concentrations. From this data, it is clear that the GRIM at room temperature and a concentration of 0.1 M are the optimal conditions for the monomer formation (Test 3 in Table 1).

Table 1. Optimization of the GRIM reaction[a,b].

Test	Reaction conditions		Composition	
	Temperature (°C)	Concentration (mol/L)	% **1**	% **2**
1	RT[c]	0.05	26	74
2	40	0.05	33	67
3	RT	0.10	5	95
4	40	0.10	28	72
5	RT	0.15	44	56

[a] GRIM reaction time = 30 min;[b] ^{1}H NMR spectra of the determination of the composition are located in the Supporting Information; [c] RT= room temperature

Homopolymerization

After the optimization of the monomer conversion, a KCTP-polymerization using a Ni(dppp)Cl_2-catalyst (2.5 mol%) (dppp = 1,3-bisdiphenylphosphino propane) was performed at room temperature (**P1**), and a $\bar{M}_n$ vs conversion as well as a $\ln\frac{[M_0]}{[M]}$ vs time plot was recorded (Figure 2) using GPC measurements. The obtained polymers, after a polymerization time of 20 min, showed a $\bar{M}_n$-value of 31.2 kg/mol. This is much higher than the expected $\bar{M}_n$ (~16 kg/mol). GPC indeed typically overestimates the molar mass of conjugated polymers, but the factor here is quite large – larger than for instance with P3HT. On the other hand, PCPDT is also more rigid than P3HT as two consecutive rings are locked, which might explain this larger overestimation. Alternatively, it might be that not all Ni(dppp)Cl_2 initiated a polymerization as it is only sparingly soluble in THF. However, when a chain extension experiment is executed (see further), no newly initiated PCPDT is found, suggesting that there is no Ni(dppp)Cl_2 left at the end of the polymerization.

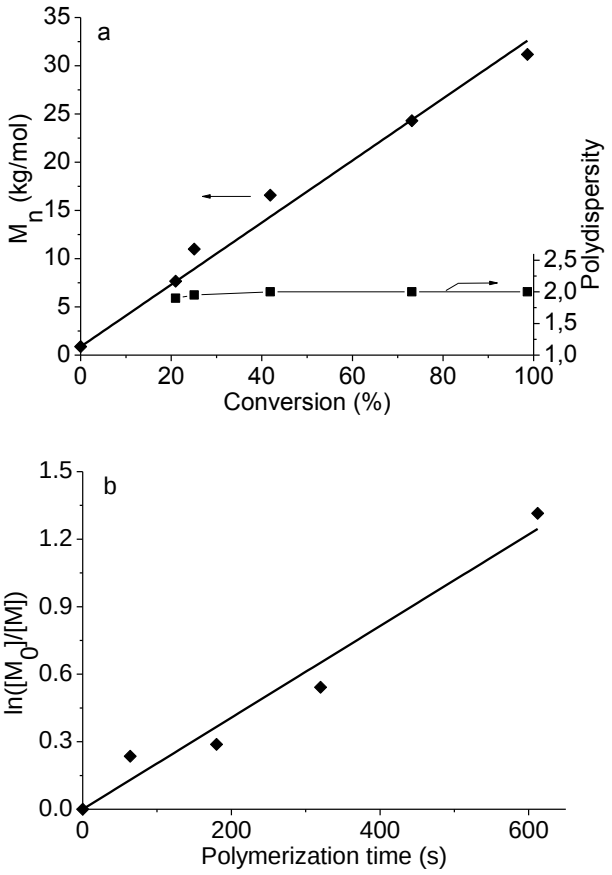
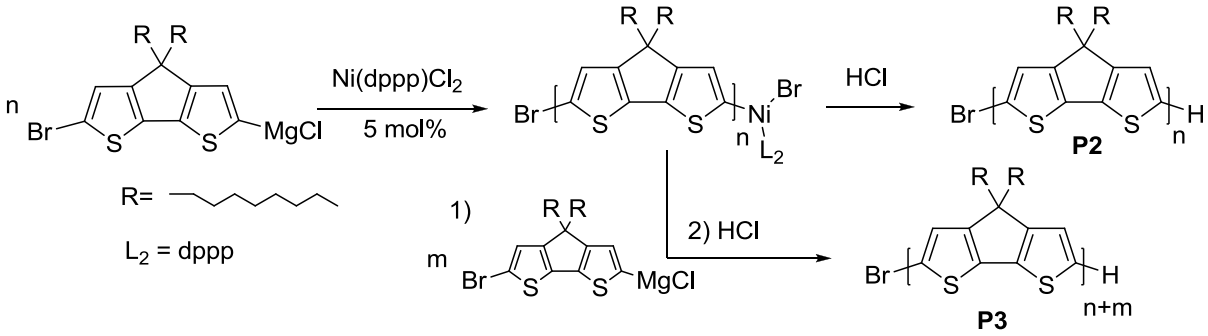


Figure 2. a) relation between $\bar{M}_n$ and conversion; b) relation between ln([M]$_0$/[M]) and polymerization time. c = 0.1 M at RT

The $\bar{M}_n$ vs conversion graph (Figure 2a) shows a clear linear relation, indicating that the polymerization proceeds via a chain-growth mechanism without visible transfer reactions. After 20 minutes, conversions close to 100% are obtained, indicating that the polymerization is completed within this time period. In the plot of $\ln\frac{[M_0]}{[M]}$ vs time (Figure 2b), a linear relation is also obtained, indicating that there are also no noticeable termination reactions taking place during the polymerization. Furthermore, this linear relationship implies that the transmetalation is the rate determining step of the polymerization, which is in line with findings of Lanni *et al*. on both thiophene and phenylene based systems if dppp is used as the catalyst ligand.[69]

In order to obtain further proof for the controlled nature of the polymerization of CPDT, a chain extension experiment was performed. Thus, after an initial polymerization time of 20 min, half the polymerization mixture was quenched with acidified THF (**P2**), whereas to the remainder, a second equivalent of CPDT-monomer was added (Scheme 2). After an additional 30 min reaction time, the complete polymerization mixture was quenched with acidified THF (**P3**). The resulting GPC traces of these polymers are depicted in Figure 3.



Scheme 2. Chain extension experiment.

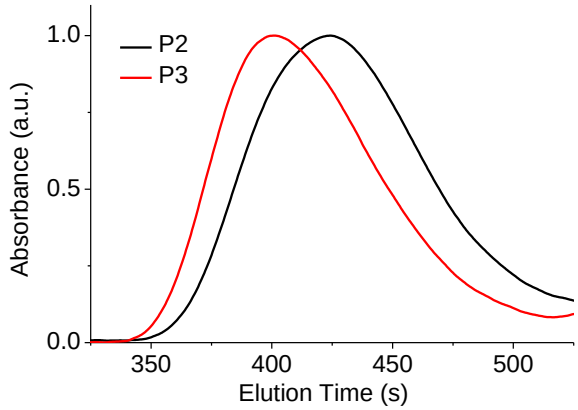


Figure 3. GPC spectra of **P2** and **P3**.

The clear shift towards lower elution time between **P2** and **P3** shows that the polymer chains undergo further growth after the addition of the second portion of the CPDT-monomer. The

GPC-spectra show an increase of the $\bar{M}_n$-value from 18.3 kg/mol to 31.1 kg/mol. Also, no bimodality is visible in the GPC spectrum of **P3**, indicating that the polymer chains are still living after 20 min polymerization. Furthermore, the polydispersity remained unchanged at 2.0, which further indicates that no new polymer chains are formed.

Next, also a MALDI-ToF spectrum of **P2** was recorded (Figure S8a). Unfortunately, the high polydispersity (see further) did not allow us to obtain a representative spectrum, as only the low molar mass fraction was ionized. Most of the peaks were indeed H/Br –terminated, as is expected if a controlled chain-growth mechanism is obtained, but also some H/H and Br/Br were found. It is however not clear whether this is only the case for the low-molar mass fraction (up to the 10-mer), or representative for the whole batch. In combination with the established linear relationship and the successful chain extension experiment, we can conclude that the majority of the chains indeed polymerize in a controlled chain-growth polymerization, but that some side reactions are however present. Moreover, a PCPDT of lower molar mass was prepared and analyzed with MALDI-ToF, which indicated that the vast majority was indeed H/Br end-capped (Figure S8b).

In the case of the Ni(dppp)-catalyzed polymerization of P3AT, it has clearly been demonstrated that the Ni-catalyst remains complexed to the growing polymer chain and that the strength of this π-complexation is a crucial parameter for the controlled nature of the polymerization.[47,70–72] Indeed, if this π-complexation is weak, the Ni-catalyst can easily dissociate from the growing polymer chain, hereby losing the controlled character. Therefore, whether the polymerization is actually living or not depends on the possibility of the catalytic Ni-moiety to 'travel' along the π-conjugated monomer, reach the terminal C-Br bond and oxidatively insert there within the lifetime that it remains complexed to the π-conjugated backbone. Given the fact that the CPDT

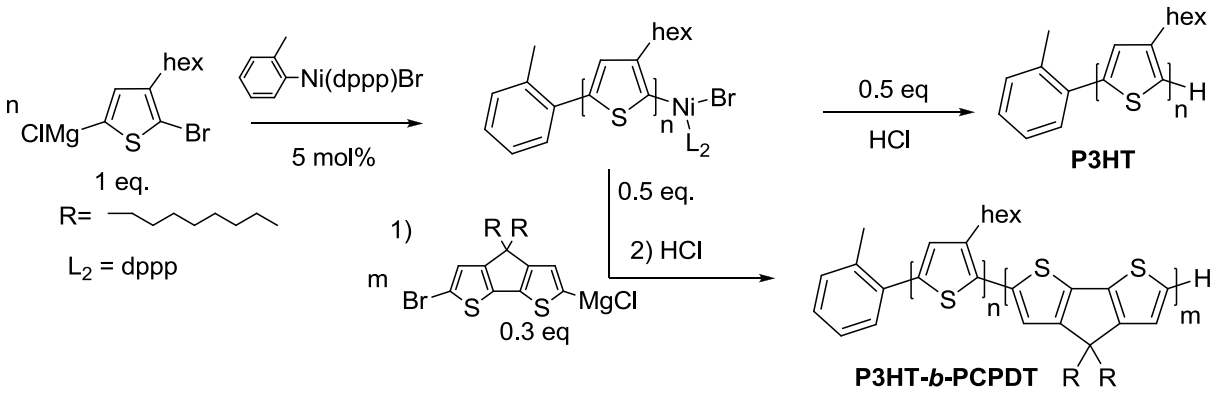
monomer is twice as long as thiophene, it could be questioned whether the polymerization proceeds without termination and transfer reactions. Indeed, it has been shown by KCTP-polymerization of bi- and terthiophene, that the chain-growth polymerization is maintained for longer monomer units, however with higher chain-transfer probabilities and, resultantly, a decreased controlled character.[73] In the case of CPDT, however, our experiments indicate that transfer and termination reactions occur only limited during the polymerization. Furthermore, after a full conversion of the first CPDT-equivalent (after 20 min), all growing polymer chains remain active and continue to grow after a second equivalent is added.

Although the previous experiments strongly indicate that the polymerization indeed follows largely a controlled chain-growth mechanism, a polydispersity (PDI) of typically 2.0 is consequently obtained, which is unusually high compared to the PDI of P3ATs prepared with Ni(dppp)Cl_2 (<1.3). The observed higher PDI does, however, not necessarily mean that transfer or termination reactions occur, but can, instead, also be ascribed to a slower initiation step compared to propagation. This hypothesis is further confirmed if an external, soluble *o*-tolyl-Ni(dppp)-Br initiator is used for the polymerization (**P4**).[74] In this case, the PDI is decreased to 1.38, indicating that it is indeed affected by the rate of the initiation. However, the use of an external initiator also results in a lower molar mass ($\bar{M}_n$ = 7.5 kg/mol) and poor monomer consumption (SI, Figure S11). Decreasing the overall concentration in order to tackle the problem of slow initiation versus propagation was not considered, since already a relative high dilution is used.

Block-copolymer formation

The fact that a controlled chain-growth mechanism for PCPDT is realized under the same polymerization conditions as for P3AT, suggests that both monomers can also be combined in

the same polymerization reaction to obtain all-conjugated block-copolymers, consisting of a PCPDT and a P3AT block. To investigate this, a **P3HT-*b*-PCPDT** block-copolymer was synthesized. An external *o*-tolyl-Ni(dppp)-initiator was used to ensure formation of a diblock-copolymer without any triblock-copolymer impurities.[47,75] To this initiator, first the 3-hexylthiophene monomer is added and after 1 h, one aliquot is quenched, while to the remainder, the CPDT-monomer is added, hereby forming the desired block-copolymer (Scheme 3).



Scheme 3. Synthesis of the **P3HT-*b*-PCPDT** block-copolymer.

The GPC traces were recorded for the **P3HT** homopolymer and the **P3HT-*b*-PCPDT** block-copolymer after Soxhlet extraction with subsequently methanol, hexane and chloroform (Figure 4). The shift to lower elution volumes clearly shows that a block-copolymer is indeed formed, although a small shoulder originating from unreacted P3HT homopolymer is present. In order to further confirm the block-copolymer formation, the GPC spectra of **P3HT-*b*-PCPDT** were also recorded at 430 nm (~ λ_{max} of P3HT) and 600 nm (~ λ_{max} of PCPDT) as well as with an refractive index detector (RID). The polydispersity of the block-copolymers was constant at 1.45 for the GPC-spectra. These experiments indeed confirm the formation of the desired block-copolymer.

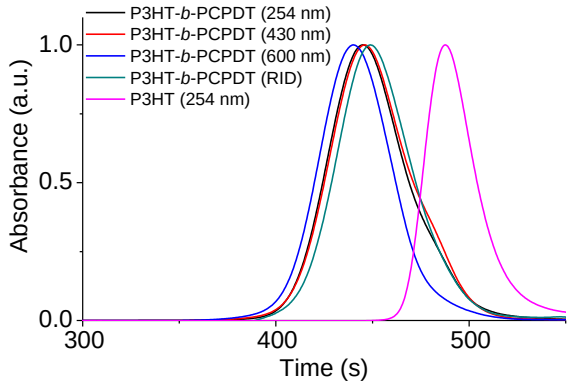


Figure 4. GPC spectra of **P3HT** and **P3HT-*b*-PCPDT**.

Although GPC can give an estimation of the molar mass, the use of polystyrene standards inevitably results in erroneous molar masses. However, end-group quantification using ^{1}H NMR spectroscopy can provide the absolute degree of polymerization (DP) of **P3HT**, and, as a consequence, also of the **P3HT-*b*-PCPDT** block-copolymer. If the region of the α-methylene protons of **P3HT** is considered (Figure 5I), the tolyl methyl, originating from the initiating species (signal c), the α-methylene protons of the terminal thiophene unit, *i.e.* the end-group (signal b), and those of the inner thiophene units (signal a) can be distinguished. The fact that the initiating and end groups have corresponding integration values, suggests a quantitative initiation of the external initiator. Moreover, the end-group corresponds to an α-methylene signal with a -H in the 2-position of the terminal thiophene and not a -Br, demonstrating that the polymerization was perfectly living when the second block was introduced.[47,76] From the ratio of terminal α-methylene and inner α-methylenes (signals b and a, respectively), the DP can be estimated to be 21, which corresponds very well to the targeted DP = 20. If the ^{1}H NMR spectrum of **P3HT-*b*-PCPDT** (Figure 5II) is considered, the α-methylene signal of the terminal thiophene disappears, indicating the block-copolymer formation. The DP of the PCPDT block can be calculated from

the relative integration of the α-methylene signals from the P3HT (signal a) and PCPDT block (signal d). This reveals a DP = 10, quite close to the expected DP of 12.

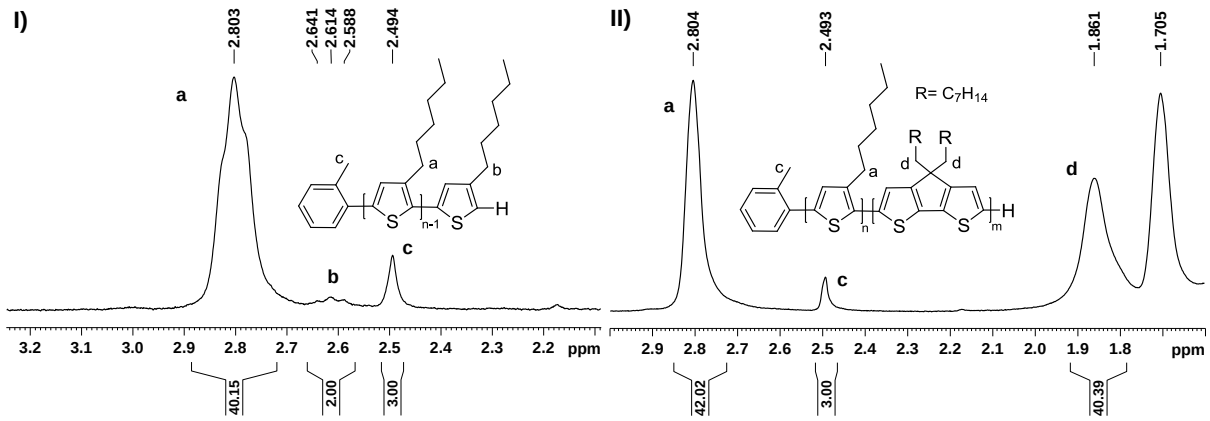
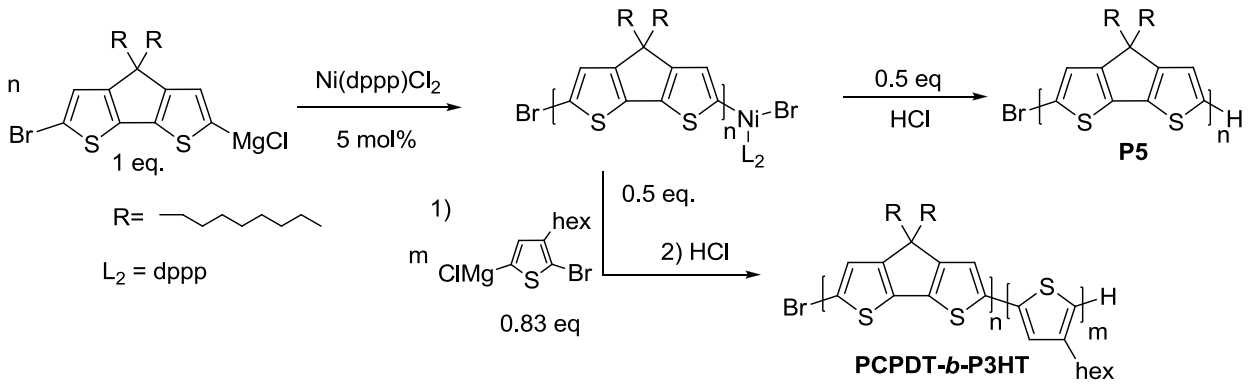


Figure 5. ^{1}H NMR spectra of the α-methylene region of I) **P3HT** and II) **P3HT-*b*-PCPDT**.

Next, it was attempted to reverse the order of monomer addition. Thus, CPDT was polymerized as the first block using Ni(dppp)Cl_2 as a catalyst/initiator. Ni(dppp)Cl_2 and not an external initiator was used, since the latter resulted in a lower control of the polymerization. Nevertheless, the formation of triblock-copolymers as a side product is not expected here, because of the more electron-rich character of the CPDT-unit in comparison with thiophene. After polymerization of the first block, an aliquot was terminated with HCl, while to the remainder the thiophene monomer was added, which should result in **PCPDT-*b*-P3HT** (Scheme 4).



Scheme 4. Synthesis of the **PCPDT-*b*-P3HT**.

A GPC-spectrum was recorded from both the PCPDT homopolymer (**P5**) and the attempted block-copolymer **PCPDT-*b*-P3HT** (Figure 6). From these spectra, it is clear that no chain extension occurred after addition of the thiophene monomer. This can be explained by the complexation of the Ni(dppp) moiety to the PCPDT polymer chain. Indeed, the groups of Yokozawa and Wang suggested that the Ni(dppp) complexes preferentially with the most electron-rich unit. [28,35,56,77] Thus, after polymerization of the P3HT homopolymer and the addition of one CPDT monomer, the Ni(dppp) moves to the more electron-rich CPDT and further growth occurs, successfully forming **P3HT-*b*-PCPDT**. However, when PCPDT is polymerized as the first block, the Ni(dppp) remains with the PCPDT and, consequently, the polymerization is stopped. A second feature that is revealed from Figure 6 is the occurrence of a peak around 475 s, which becomes very pronounced when the detection is done at 430 nm, but is absent at 600 nm. This strongly indicates that this corresponds to the formation of P3HT homopolymer. This can be explained by some dissociation of the Ni(dppp)-catalyst from the PCPDT homopolymer, which reacts with the thiophene monomers, starting the homopolymerization of the P3HT. Alternatively, it might also be that not all Ni(dppp)Cl_2 had reacted in the PCPDT homopolymerization – the PCPDT polymerization proceeds quite fast and Ni(dppp)Cl_2 dissolves poorly – and that the remaining Ni(dppp)Cl_2 initiated the P3HT homopolymerization, however this possibility is less likely if we consider the successful chain extension experiment.

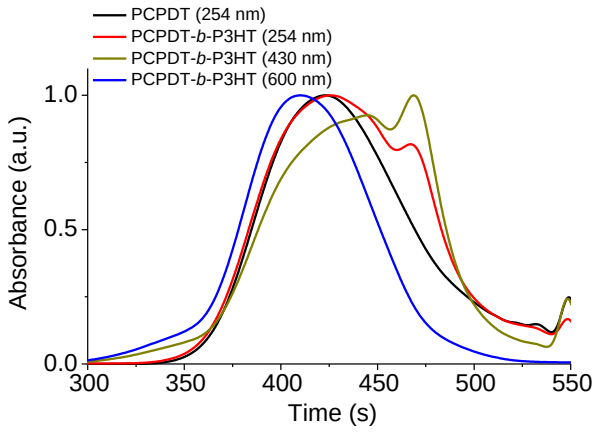
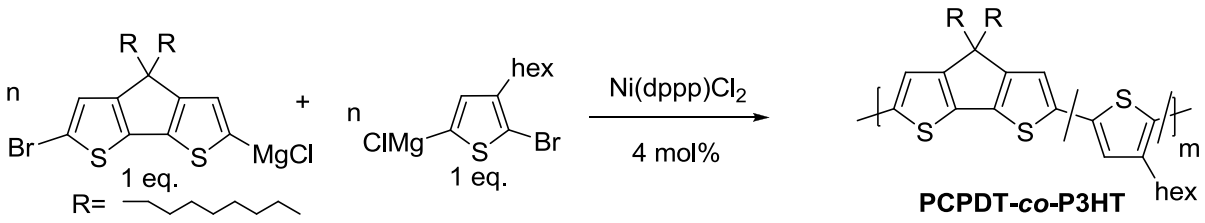


Figure 6. GPC spectra of **PCPDT** and **PCPDT-*b*-P3HT**.

In order to further prove that a growing CPDT chain-end cannot react with 3-hexylthiophene monomer, a random copolymerization of both these monomers was attempted (Scheme 5). The crude polymerization mixture was investigated by GPC (Figure 7), which revealed the presence of large amounts of remaining monomers (peaks at 570 and 610 s) and a multimodal peak, composed of two different oligomers and one higher-molar mass fraction. The failure to produce a monomodal GPC spectrum originating from a random copolymer further confirms the hypothesis.



Scheme 5. Synthesis of the **PCPDT-*co*-P3HT**.

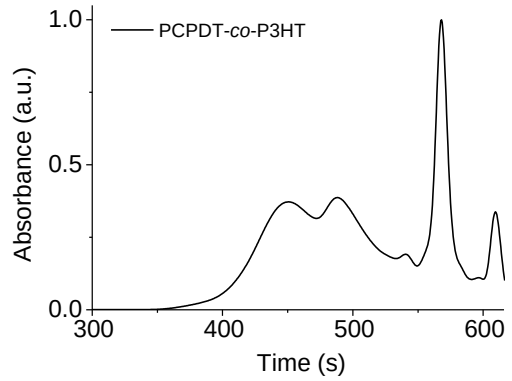


Figure 7. GPC spectra of **PCPDT-*co*-P3HT**.

UV-vis and DSC characterization

From the **P3HT-*b*-PCPDT** block-copolymer, a UV-vis spectrum was recorded in good solvent ($CHCl_3$) (Figure 8). Also a spectrum of the corresponding **P3HT** homopolymer and **P1** were recorded. Since the mass fractions of both blocks can easily be calculated from the known DPs of both blocks, a UV-vis spectrum of the **P3HT-*b*-PCPDT** block-copolymer can be simulated assuming that both blocks do not electronically influence each other. However, the difference between the recorded and simulated spectrum for **P3HT-*b*-PCPDT** suggest that there is some electronic interaction between both blocks. This can be correlated with the fact that the junction between both blocks corresponds to a normal HT-dyad of thiophene, of which it is known that conjugation is present.

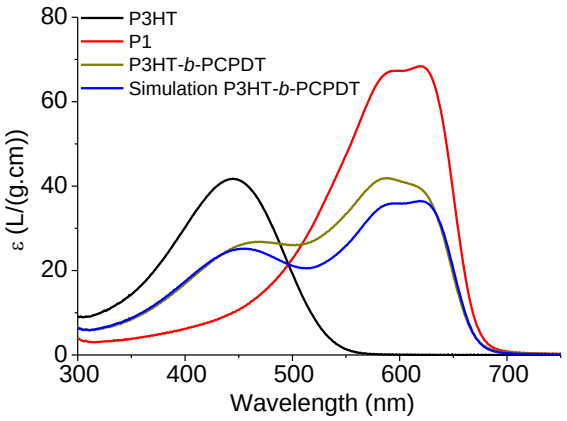


Figure 8. UV-vis spectra of **P3HT** and **P1** homopolymers and the recorded and simulated spectra of the corresponding **P3HT-*b*-PCPDT** block-copolymer.

Finally, DSC spectra were recorded of the **P3HT**, **P1** and **P3HT-*b*-PCPDT** (Figure 9). Typically, the second heating scan (10 °C/min) after curing at 210 °C for 15 min was considered. In correspondence with previously obtained data,[67] the **P1** homopolymer did not show a melting peak nor a clear T_g, while **P3HT** showed a melting peak at 187°C and a ΔH_m of 9.3 J/g. If the DSC spectrum of the **P3HT-*b*-PCPDT** block-copolymer is considered, a melting peak of the P3HT block was observed 8 °C lower than in the **P3HT** homopolymer and its melting enthalpy was also decreased. Taking into account the "dilution" with PCPDT (53.3 m%), a ΔH_m of ~4.3 J/g would be expected while a ΔH_m of ~3.0 J/g is found, demonstrating that the presence of the PCPDT block hampers the crystallization of the P3HT block. This also explains the reduction of T_m, as less perfect crystals are formed.

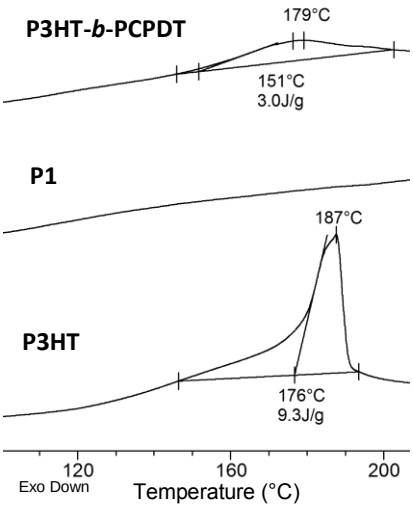


Figure 9. DSC spectra of **P3HT**, **P1** and **P3HT-*b*-PCPDT**. The second heating scan (10 °C/min) is shown.

CONCLUSION

In this paper, we have investigated the nature of the KCTP-polymerization of cyclopenta[2,1-*b*;3,4-*b'*]dithiophene (CPDT) using Ni(dppp)Cl_2. It is shown that this monomer polymerizes in a controlled chain-growth fashion. This was shown by linear relationships between the $\bar{M}_n$ and conversion as well as between the $\ln\frac{[M_0]}{[M]}$ and polymerization time. The polymerization proved to proceed very fast with high conversions of almost 100% after a polymerization time of 20 minutes. In combination with a relatively slow initiation with Ni(dppp)Cl_2, this leads to higher polydispersities (± 2.0). Nonetheless, it was shown that the majority of the chains was still living after this period, as a complete chain-extension was observed after addition of new monomer. Also a one-pot synthesis of all-conjugated block-copolymers consisting of a P3HT and a PCPDT block was investigated. A P3HT-*b*-PCPDT block-copolymer was readily formed with great control over the length of the constituting blocks. On the other hand, we were unable to synthesize a PCPDT-*b*-P3HT block-copolymer, with the CPDT block as the first block. This

observation is in line with previous findings, as the Ni(dppp) catalyst remains complexed to the most electron-rich block, *i.e.* CPDT.

ASSOCIATED CONTENT

Supporting Information. Used instrumentation and experimental details, ^{1}H NMR spectra of the GRIM tests and of the polymers, a $\overline{M}_n$ vs time curve of **P1**, the MALDI-Tof MS spectrum and crude GPC spectra of **P3HT-*b*-PCPDT** are included in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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